Further studies on silatropic carbonyl ene cyclisations: β-crotyl(diphenyl)silyloxy aldehyde substrates; synthesis of 2-deoxy-2-*C*-phenylhexoses†

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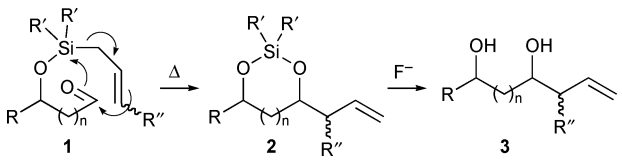
Silatropic carbonyl ene cyclisations of β-(allylsilyloxy)- and β-(crotylsilyloxy)butyraldehydes are shown to proceed with high stereoselectivity but at a much reduced rate in comparison to the cyclisation of analogous α-substrates. In the second section, olefin cross-metathesis is explored as a route to substituted α-(allylsilyloxy)aldehydes and the method applied to the synthesis of diastereomeric 2-deoxy- and 2-deoxy-2-*C*-phenyl hexose derivatives from butanediacetal-protected D-glyceraldehyde.

Introduction

Within our programme exploring stereoselective syntheses of non-natural carbohydrate analogues we discovered that heating α-dialkyl(allylic)silyloxy aldehydes (**1**, $n = 0$) induced intramolecular transfer of the allylic group to yield *syn*-1,2-dihydroxypent-4-enes (**3**, $n = 0$) after cleavage of the silyl tether.[1] This silatropic carbonyl ene cyclisation was found to be stereospecific and highly stereoselective, and we reported its application to the stereocontrolled synthesis of carbasugars and hydroxylated piperidines.[2] Mechanistically, we view this allylic transfer to occur in concert with Si–O bond formation as depicted in Scheme 1.



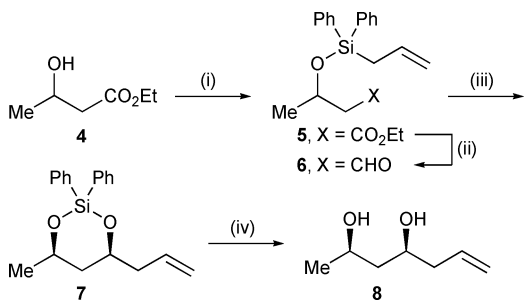
Scheme 1 Alkenyl diols formed by silatropic ene cyclisation.

To conclude our investigations of the silatropic carbonyl ene cyclisation, we report the reactions of β-silyloxy aldehyde substrates (**1**, $n = 1$), and the application of our original α-allyl transfer reaction in the synthesis of *C*-aryl sugar analogues.

Results and discussion

β-Silyloxy substrates

Reetz provided the earliest direct precedent for silicon-tethered allylation processes in a study of intramolecular allylations of β-(allylsilyl)oxyaldehydes under Lewis-acidic conditions.[3] In that work the product stereochemistry was shown to depend on the choice of Lewis acid, and crotyl systems were not examined. For our study, the unsubstituted allyl substrate **6** (Scheme 2) was prepared from (±)-ethyl 3-hydroxybutyrate by DIBAL reduction of ester **5** that was obtained using allyldiphenylsilane[4] directly[5] or by base-mediated silylation with allyldiphenylchlorosilane[6] prepared *in situ*. In general, the β-systems were much easier to handle than the α-analogues prepared in our earlier work; in particular, the DIBAL reductions provided the aldehydes reproducibly in high yield as stable compounds that could be purified or stored for prolonged periods without decomposition.



Scheme 2 *Reagents and conditions*: (i) allyldiphenylsilane, 5% $B(C_6F_5)_3$, CH_2Cl_2, reflux, 2 h (88%); (ii) DIBAL, CH_2Cl_2, −78 °C, 1 h (74%); (iii) C_6H_6, 200 °C (sealed tube), 5 d (52%); (iv) KF, MeOH, RT, 16 h (55% from **6**).

Inevitably, the stability of these aldehydes was carried forward into their behaviour towards heating, there being little tendency to rearrange to the allyl transfer products under conditions previously successful for the α-cases. For example, with aldehyde **6**, heating at 200 °C in a sealable tube for 5 days was required in order to effect complete conversion to dioxasilinane **7**. The protracted reaction time for this process led to some decomposition of the

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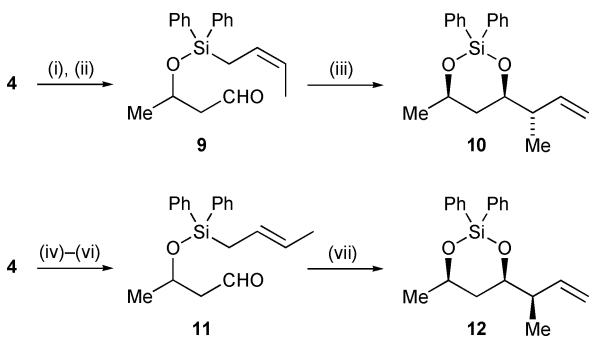
† Electronic supplementary information (ESI) available: Full experimental procedures and characterisation data for all compounds **5**, **6**, **9** (and intermediates), **11** (and intermediates), **15**, **20**–**24**, **31**/**32** and **43**/**44**, **37**/**38** and **49**/**50**, **39**/**40** and **51**/**52**; crystal structure data. See DOI: 10.1039/b804752a

substrate and the silacycle could be isolated only in moderate yield. In later work (discussed below), thorough base-washing of the reaction tubes and replacement of the O-ring with PTFE tape reduced the amount of decomposition with the consequence that isolated yields were raised by *ca.* 10–15%. The isolated silacycle **7** was confirmed as the diastereoisomer depicted in Scheme 2; thus, in the ^{1}H NMR spectrum the coupling constants (Hz) for the ring methylene protons supported diequatorial substitution around the ring (δ 1.69: dt, J 14.0, 10.5, CH_{ax}H; δ 1.78: dt, J 14.0, 2.5, CHH_{eq}). In a separate experiment, direct desilylation of the crude silacycle gave *syn*-1,3-diol **8**[7] in 55% yield from aldehyde **6**.

Extension to the crotyl precursors proceeded very well by our previously developed methodology (Scheme 3), and single diastereomers of the methallyl-substituted dioxasilinanes **10** and **12** were obtained in 63% and 68% yields respectively (*ca.* 45% overall yield from ethyl 3-hydroxybutyrate). Once more, the coupling constants for the ring methylene protons in the ^{1}H NMR spectra of these silacycles supported a diequatorial substitution pattern (see Experimental section for details). Furthermore, X-ray-quality crystals of silacycle **12** were grown in order to assign the allylic stereochemistry in this compound (Fig. 1) and, by analogy, in diastereomer **10**; this also assisted in securing the assignment of compound **7** by correlation.[8]



Scheme 3 *Reagents and conditions*: (i) (*Z*)-crotyldiphenylsilane, 5% $B(C_6F_5)_3$, CH_2Cl_2, reflux, 2 h (71%); (ii) DIBAL, CH_2Cl_2, −78 °C, 1 h (96%); (iii) C_6H_6, 200 °C (sealed tube), 5 d (63%); (iv) 3-butenyldiphenylsilane, 5% $B(C_6F_5)_3$, CH_2Cl_2, reflux, 2 h (88%); (v) 1% $[(COD)Ir(PPh_2Me)_2]^+$ PF_6^-, (H_2), CH_2Cl_2,–78 → 0 °C, 20 min., (99%); (vi) DIBAL, CH_2Cl_2,–78 °C, 1 h (79%); (vii) C_6H_6, 200 °C (sealed tube), 5 d (68%).

An attempt to rationalise the stereochemical outcome in these reactions is presented in Fig. 2. A pre-transition-state assembly can be considered that consists of a forming bicyclo[3.3.1]nonane ring in which the ring containing the transferring allylic group is initially chairlike whilst the forming dioxasilinane adopts a flattened half-chair conformation (**A** and **B**). Although the longer bonds to silicon[9] should allow some relaxation of transannular interactions in these assemblies, the carbon that bears the Me-group must adopt an *exo*-position; in the *endo* position, the attached Me substituent or the H atom will suffer an unfavourable interaction with the central olefinic methine. Of the two possibilities, conformation **B** appears to be disfavoured because the pseudoaxial Me substituent is brought into close contact with the "axial" phenyl group attached to the trigonal bipyramidal silicon atom.[10]

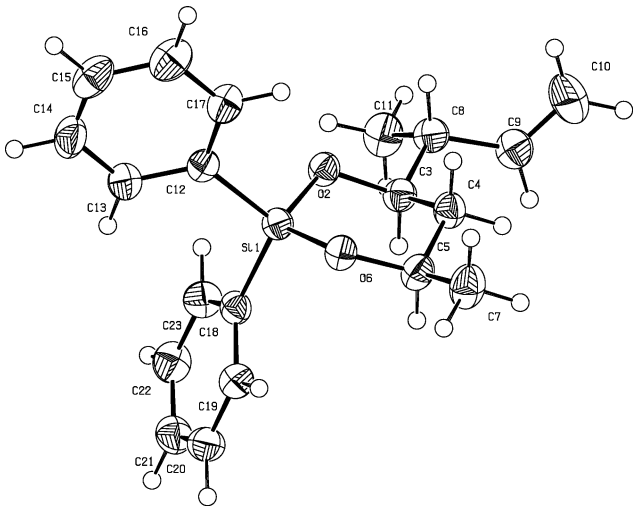


Fig. 1 ORTEP diagram of dioxasilinane **12**.

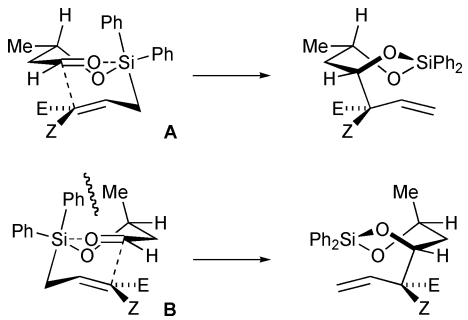
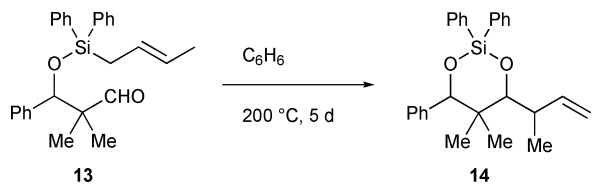


Fig. 2 Pre-transition-state assemblies for cyclisation of β-substrates.

Heating α,α-dimethyl-substituted analogue **13**[11] (Scheme 4) at 200 °C for 5 days resulted in an incomplete reaction (**14**/**13**, 3.25 : 1). We assume that any entropic advantage offered by the presence of the *gem*-dimethyl group is offset by steric encumbrance at the carbonyl group. Furthermore, the dioxasilinane (**14**) was produced as a 2.5 : 1 ratio of diastereomers as determined by examination of relative integrations of the newly-formed C*H*O resonances in the ^{1}H NMR spectrum of the crude material.

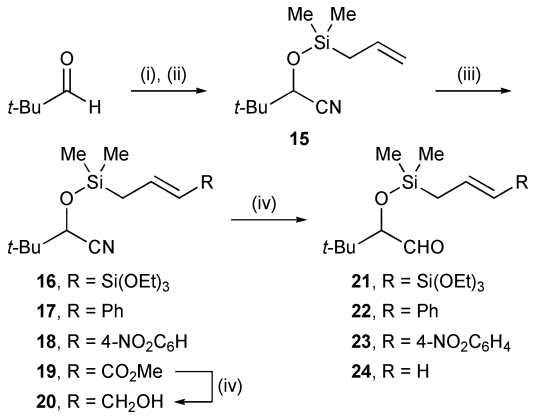


Scheme 4 Cyclisation of a *gem*-dialkyl-substituted substrate.

α-Cinnamyl(diphenyl)silyloxy substrates: application to 2-deoxy-2-*C*-phenylhexoses

In order to complete our study of the scope and potential synthetic applications of allylic transfer by silatropic carbonyl ene cyclisation we sought a flexible synthesis of allylic substrates bearing a variety of 3-substituents (**1**, Scheme 1, $n = 0$, $R'' \neq H$). Given the ease of preparation of allyl substrates (R = H), olefin cross-metathesis[12] was investigated as a means of accessing the

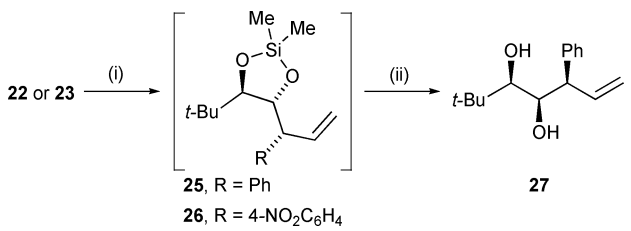
functionalised allylic variants.[13] Most of our work prior to this point had employed a relatively stable diphenylsilyl tether, which required the preparation of fresh allyldiphenylchlorosilane; in view of this, and given the commercial availability of allyldimethylchlorosilane, we decided to explore the cross-metathesis chemistry on substrate **15** (Scheme 5).



Scheme 5 *Reagents and conditions*: (i) KCN, $NaHSO_3$, H_2O, THF (87%); (ii) allyldimethylchlorosilane, Et_3N, DMAP, DMF, 60 °C, 6 h (83%); (iii) (a) →**16**: 5 eq. triethoxyvinylsilane, 10% Grubbs II, CH_2Cl_2, reflux, 21 h (34%); (b) →**17**: as (a) but with 1 eq. styrene, 18 h (51%); (c) →**18**: as (b) but with 4-nitrostyrene (40%); (d) →**19**: as (b) but with methyl crotonate (44%); (iv) DIBAL, CH_2Cl_2,–78 °C, 1 h (**19**→**20**, 46%; **16**→**21**, 14%; **17**→**22**, 30%; **18**→**23**, 66%; **15**→**24**, 64%).

Preliminary experiments established that the presence of the nitrile functionality in this substrate (**15**) necessitated reasonably high catalyst loadings in order to drive the cross-metatheses to completion but, even under the optimised conditions, isolated yields were moderate at best and in some cases the products could not be separated from other components in the reaction mixtures.[14] Also, the relative fragility of the dimethylsilyl tether was revealed in the subsequent DIBAL reaction to unmask the aldehyde, and the isolated yields of the ene substrates **21**–**24** fell away drastically in the more electron-rich examples. In the case of substrate **19** reduction took place preferentially at the ester to give the primary alcohol **20** as the sole isolated product.

Although these substrates were hydrolytically sensitive, the neutral, thermal conditions required for silatropic ene reaction were sufficiently mild to allow the silacycles to form smoothly and the progress of the reactions to be monitored by ^{1}H NMR spectroscopy (Scheme 6). The presence of the phenyl group slowed the cyclisation of substrate **22** relative to that of substrate **24** and the reaction required 84 h at 80 °C to reach completion (*vs.* 48 h for **24**).[15] In this example diol **27** was obtained as a single

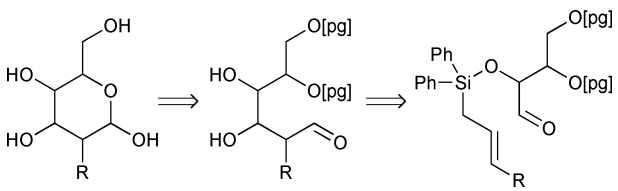


Scheme 6 *Reagents and conditions*: (i) C_6H_6, 80 °C, 3.5 d (→**25**) or 8 d (→**26**); (ii) TBAF, THF, 0 °C → RT, 2 h (56% from **22**).

diastereomer after cleavage of the silyl tether (stereochemistry assumed by analogy to previous work). Cyclisation of the 4-nitrophenyl derivative **23** was incomplete even after 8 d; regardless, a single attempt to cleave the small available amount of (nitrophenyl)allyl transfer product **26** resulted in fragmentation to give 1-(4-nitrophenyl)propene.[16]

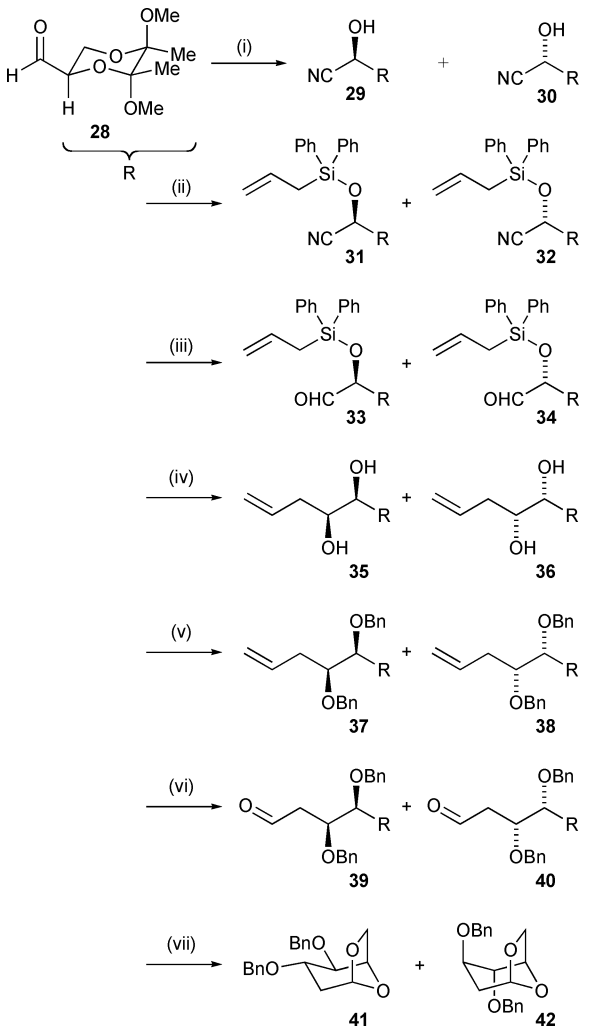
This exploratory work had shown that the basic synthetic plan was viable but also that the overall yields were unacceptably low, largely as a consequence of the DIBAL reduction step; therefore, subsequent work returned to the more resilient diphenylsilyl-tethered substrates. With the intention of exploring the potential of these allyl transfer processes to deliver enantiomerically pure carbohydrate analogues,[17] we initiated studies to outline the synthetic route and assess the stereochemical aspects in a relatively simple system.

We envisaged that if the chemistry in Schemes 5 and 6 could be achieved with an enantiomerically pure masked diol fragment in place of the *tert*-butyl group then ozonolysis of the silatropic ene product and liberation of the diol would yield a variety of 2-deoxy-2-*C*-substituted sugars (Scheme 7, *e.g.* R = phenyl). This class of carbohydrate analogues has been accessed by organometallic opening of 2,3-anhydro sugars. In the earlier literature the regio- and stereochemical features of these reactions were somewhat vague, and the nature of the products was found to vary depending on the organometallic reagent.[18] More recently, the use of cuprates was shown to provide reliable results, but only in pyranosides in which the epoxide and anomeric substituents are present in a *cis*-relationship.[19] Our study was therefore formulated to provide a stringent test of the silatropic ene chemistry and to enable a flexible and complementary route to these useful carbohydrate analogues.



Scheme 7 An approach to 2-deoxy-2-*C*-substituted sugars.

Aldehyde **28**[20] (Scheme 8) was converted into a 3 : 2 mixture of cyanohydrins **29** and **30** whose stereochemistry was assigned retrospectively, as explained below. Ene substrates **33** and **34** were then prepared straightforwardly by the usual silylation and DIBAL reduction sequence. We were pleased to find that heating these functionalised substrates in benzene produced protected tetraols **35** and **36** with complete stereocontrol.[21] Ozonolysis of these dihydroxyaldehydes proceeded poorly; therefore the diol was benzylated to enable aldehydes **39** and **40** to be obtained cleanly. Final cleavage of the butanediacetal (BDA) group, under the standard TFA conditions,[22] proved to be problematic as the products decomposed when concentrated in the presence of acid. Therefore, intending to minimise potential product isolation problems associated with an aqueous work-up, we opted for a 90 : 9 : 1 mixture of 1,2-dichloroethane–TFA–water;[23] this allowed selective removal of most of the TFA before the mixture was finally concentrated, and pyranose products **41** and **42** were isolated, albeit in rather low yield. In later work we found much improved conditions for BDA deprotections but did not go back to repeat this exploratory sequence merely to improve yields. The products

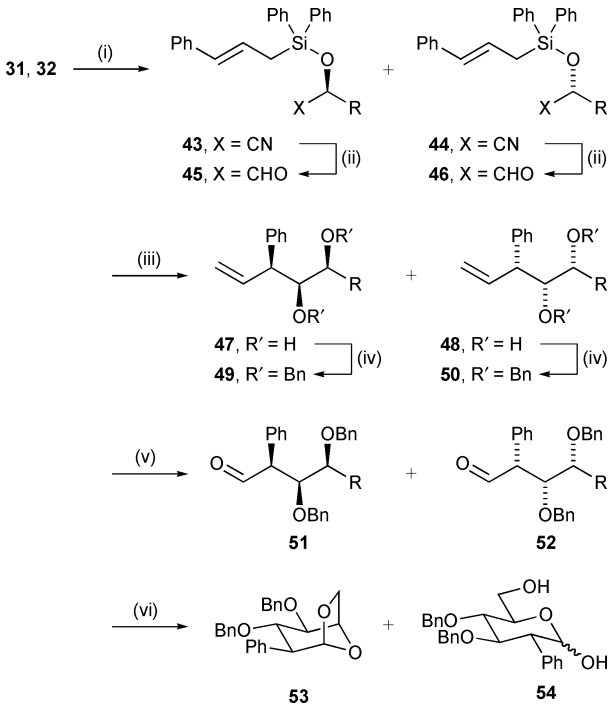


Scheme 8 *Reagents and conditions*: (i) KCN, $NaHSO_3$, H_2O, THF (87%, 3 : 2 ratio); (ii) allyldiphenylchlorosilane, Et_3N, DMAP, DMF, 60 °C, 6 h (80%); (iii) DIBAL, CH_2Cl_2, −78 °C, 1 h; (iv) C_6D_6, 80 °C, 16 h then TBAF, THF, 0 °C → RT, 2 h (24% from **31**/**32**); (v) NaH, TBAI, benzyl bromide, DMF, 0 °C → RT, 16 h (65%); (vi) O_3, CH_2Cl_2,–78 °C then Me_2S, −78 °C → RT, 5 h (89%); (vii) TFA, H_2O, 1,2-dichloroethane, RT, 2 min, (**41**, 9%; **42**, 12%).

2-deoxy-D-*gulo*-**41** and 2-deoxy-D-*gluco*-**42**[24] (1 : 1.5 ratio) were both obtained in the 1,6-*anhydro*- form, the stereochemistry being readily assigned in these rigid structures by coupling constant analysis (see Experimental section).

The stereochemistry of the various intermediates in this sequence was assigned as follows: in the reaction to produce diol mixture **35**/**36** a small amount of one of the isomers was obtained as a pure compound. This was then taken through the benzylation, ozonolysis and deprotection sequence to result in compound **42**. This, in turn, assigned the separated isomer as compound **36** which, based on the isomer ratios, allowed an assignment of NMR resonances to specific stereoisomers in compounds **29**/**30** → **39**/**40**.

Finally, the sequence was repeated with the inclusion of a cross-metathesis step with styrene (Scheme 9). This time the 4,6-diol in aldehydes **51** and **52** was revealed by heating with aqueous acetic acid[25] to generate two pyranose products in good overall yield,



Scheme 9 *Reagents and conditions*: (i) styrene, 7.5% Grubbs II, CH_2Cl_2, reflux, 18 h (51%); (ii) DIBAL, CH_2Cl_2, −78 °C, 1 h; (iii) C_6D_6, 80 °C, 5 d then TBAF, THF, 0 °C → RT, 2 h (25% from **43**/**44**); (iv) NaH, TBAI, benzyl bromide, DMF, 0 °C → RT, 16 h (66%); (v) O_3, CH_2Cl_2,–78 °C then Me_2S, −78 °C → RT, 5 h (81%); (vi) AcOH, H_2O, 100 °C, 2 h (**53**, 47%; **54**, 27%).

the major product being the D-*ido*-isomer **53**. The minor (D-*gluco*-configured) product (**54**), was isolated as a *ca.* 1 : 1 mixture of anomers rather than the 1,6-*anhydro*-derivative; as expected, the penalty for placing a phenyl and two benzyloxy substituents in an axial disposition is clearly too great for this compound to cyclise under the reaction conditions.

Conclusions

These results confirm that the silatropic carbonyl ene cyclisation proceeds under neutral conditions with high and predictable stereoselectivity even with β-derivatives and aryl-substituted α-derivatives. We have shown that the products may be elaborated in a synthetically useful manner, in this case to a variety of hexose derivatives, and that the main limitation to the methodology lies in the inefficiency of the DIBAL reduction used to prepare the aldehyde ene substrates.

Experimental

General procedure for allyl transfer reactions of aldehydes 6, 9 and 11

A solution of the aldehyde (0.46–1.08 mmol) in benzene (10 mL) was placed in a sealed tube and heated at 200 °C for 5 days on a Wood's metal bath with periodic monitoring by ^{1}H NMR spectroscopy. The reaction mixture was cooled and the solvent removed *in vacuo*. The resulting oil was purified by column chromatography (petrol–ether, 25 : 1).

(4*R,6*S**)-*cis*-4-Allyl-6-methyl-2,2-diphenyl[1,3,2]dioxasilinane (7).** From aldehyde **6** (1.0 mmol) the general procedure gave the *title compound* (**7**, 161 mg, 52%) as a colourless oil. R_f 0.53 (petrol–ether, 10 : 1); ν_{max}/cm^{-1} (film) 3070m, 3050w, 3003w, 2973m, 2932m, 2902m, 2862m, 1642w, 1592w, 1430s, 1377m, 1348m, 1242w, 1116s, 1024m, 980s, 925m, 910m, 871w, 848w, 786w, 739s, 719s, 699s; δ_H (400 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 6.2, CH_3), 1.69 (1 H, dt, *J* 14.0, 10.5) and 1.78 (1 H, dt, *J* 14.0, 2.5, 5-CH_2), 2.31–2.38 (1 H, m) and 2.45–2.52 (1 H, m, C*H*$_2$CH=), 4.20–4.26 (1 H, m, 4-H), 4.29–4.37 (1 H, m, 6-H), 5.10–5.18 (2 H, m, =CH_2), 5.93 (1 H, dddd, 17.2, 10.2, 7.3, 6.7, C*H*=CH_2), 7.36–7.53 (6 H, m) and 7.64–7.77 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 24.6 (q), 42.8 (t), 43.5 (t), 70.2 (d), 73.4 (d), 117.2 (t), 127.8 (d), 128.0 (d), 130.4 (d), 130.7 (d), 133.2 (s), 133.4 (s), 134.4 (d), 134.5 (d), 134.8 (d); *m*/*z* (CI$^+$) 328 (MNH_4^+, 78%), 311 (MH^+, 100), 269 (74), 250 (9), 216 (35), 198 (14); HRMS (CI$^+$) 311.1473 (MH^+. $C_{19}H_{23}O_3Si$ requires 311.1467).

(4*R,6*R**,3′*S**)-4-Methyl-6-(but-1-en-3-yl)-2,2-diphenyl[1,3,2]-dioxasilinane (10).** From aldehyde **9** (1.08 mmol) the general procedure gave the *title compound* (**10**, 219 mg, 63%) as a white crystalline solid, mp 59 °C. R_f 0.54 (petrol–ether, 10 : 1); ν_{max}/cm^{-1} (film) 3070m, 3006m, 2971s, 2930m, 2868m, 1641w, 1592m, 1457w, 1442w, 1430s, 1377s, 1347m, 1259w, 1227w, 1148s, 1116s, 1081s, 1026s, 980s, 913s, 886s, 839w, 813w, 772w, 739s, 719s, 699s; δ_H (400 MHz; $CDCl_3$) 1.15 (3 H, d, *J* 6.9, 3′-CH_3), 1.35 (3 H, d, *J* 6.1, 4-CH_3), 1.63 (1 H, dt, *J* 14.0, 2.2) and 1.75 (1 H, dt, *J* 14.0, 11.0, 5-CH_2), 2.34–2.42 (1 H, m, 3′-H), 4.10 (1 H, ddd, *J* 11.0, 4.0, 2.2, 6-H), 4.26–4.34 (1 H, dqd, *J* 11.0, 6.1, 2.2, 4-H), 5.06–5.11 (2 H, m, =CH_2), 5.91–5.99 (1 H, m, C*H*=CH_2), 7.37–7.50 (6 H, m) and 7.61–7.75 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 15.5 (q), 24.6 (q), 40.9 (t), 44.2 (d), 70.2 (d), 76.9 (d), 115.0 (t), 127.8 (d), 128.0 (d), 130.3 (d), 130.6 (d), 133.2 (s), 133.3 (s), 134.4 (d), 134.8 (d), 140.1 (d); *m*/*z* (CI$^+$) 342 (MNH_4^+, 61%), 325 (MH^+, 100), 269 (64), 216 (22), 198 (10); HRMS (CI$^+$) 325.1637 (MH^+. $C_{20}H_{25}O_2Si$ requires 325.1624).

(4*R,6*R**,3′*R**)-4-Methyl-6-(but-1-en-3-yl)-2,2-diphenyl[1,3,2]-dioxasilinane (12).** From aldehyde **11** (0.46 mmol) the general procedure gave the *title compound* (**12**, 102 mg, 68%) as a white crystalline solid, mp 48 °C. R_f 0.61 (petrol–ether, 10 : 1); ν_{max}/cm^{-1} (film) 3070m, 3050m, 2970s, 2868m, 1641w, 1592m, 1487w, 1456m, 1430s, 1370s, 1346m, 1217w, 1164s, 1116s br, 1066m, 1035m, 981s, 913s, 885s, 822m, 770w, 739s, 719s, 699s, 679w; δ_H (400 MHz; $CDCl_3$) 1.14 (3 H, d, *J* 6.7, 3′-CH_3), 1.33 (3 H, d, *J* 6.1, 4-CH_3), 1.63 (1 H, ddd, *J* 14.3, 11.0, 10.6) and 1.76 (1 H, dt, *J* 14.3, 2.1, 5-CH_2), 2.35 (1 H, dquin, *J* 7.6, 6.7, 3′-H), 3.94 (1 H, ddd, *J* 11.0, 6.7, 2.1, 6-H), 4.26 (1 H, dqd, *J* 10.6, 6.1, 2.1, 4-H), 5.02 (1 H, ddd, *J* 10.3, 1.8, 1.2) and 5.08 (1 H, ddd, *J* 17.3, 1.8, 1.1, =CH_2), 5.81 (1 H, ddd, *J* 17.3, 10.3, 7.6, C*H*=CH_2), 7.33–7.48 (6 H, m) and 7.60–7.71 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 15.6 (q), 24.6 (q), 41.5 (t), 45.0 (d), 70.3 (d), 77.1 (d), 114.9 (t), 127.8 (d), 128.0 (d), 130.3 (d), 130.6 (d), 133.4 (s), 133.5 (s), 134.7 (d), 134.8 (d), 140.6 (d); *m*/*z* (CI$^+$) 342 (MNH_4^+, 38%), 325 (MH^+, 100), 269 (75), 216 (30), 198 (8), 109 (5); HRMS (CI$^+$) 325.1624 (MH^+. $C_{20}H_{25}O_2Si$ requires 325.1624).

(2*R,4*S**)-Hept-6-ene-2,4-diol[7] (8).** A solution of aldehyde **6** (207 mg, 0.67 mmol) in benzene (10 mL) was placed in a sealed tube and heated at 200 °C for 5 days on a Wood's metal bath with periodic monitoring by ^{1}H NMR spectroscopy. The reaction mixture was cooled and the solvent removed *in vacuo*. The resulting oil was dissolved in a solution of potassium fluoride (80 mg, 1.38 mmol) in methanol (10 mL) then the mixture was stirred for 16 h and poured into water (10 mL). The solution was extracted with ethyl acetate (2 × 20 mL) and the combined extracts were washed with brine (10 mL) then dried over magnesium sulfate. The solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (petrol–ether, 3 : 2) to give the title compound (**8**, 48 mg, 55%) as a colourless oil. R_f 0.11 (petrol–ether, 1 : 1); ν_{max}/cm^{-1} (film) 3351s br, 2968s, 2933s, 1642m, 1433m, 1375m, 1325m, 1262m, 1080s, 1020m, 998m, 916m, 880w, 823w; δ_H (400 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 6.2, CH_3), 1.52 (1 H, dt, *J* 14.5, 9.9) and 1.61 (1 H, dt, *J* 14.5, 2.5, 3-CH_2), 2.18–2.31 (2 H, m, C*H*$_2$CH=), 2.94 (1 H, br s) and 3.06 (1 H, br s, 2 × OH), 3.88–3.94 (1 H, m) and 4.02–4.10 (1 H, m, 2 × C*H*(OH)), 5.11–5.16 (2 H, m, =CH_2), 5.76–5.87 (1 H, m, C*H*=CH_2); δ_C (100 MHz; $CDCl_3$) 24.1 (q), 42.6 (t), 44.1 (t), 68.9 (d), 71.8 (d), 118.4 (t), 134.2 (d); *m*/*z* (CI+) 146 (MNH_4^+, 6%), 131 (MH^+, 100), 113 (6), 95 (8); HRMS (CI$^+$) 131.1068 (MH^+. $C_7H_{15}O_2$ requires 131.1072).

General cross-metathesis procedure, used to prepare substituted allylic derivatives 16–19

To a stirred, degassed solution of silylcyanohydrin **15** (100 mg, 0.48 mmol) and the relevant alkene (see below for relative quantities) in dichloromethane (4.0 mL) was added Grubbs' second-generation catalyst (41 mg, 0.048 mmol). The reaction mixture was heated at reflux for 18 h, cooled to RT, and the solvent removed *in vacuo*; the residue was purified by column chromatography (petrol–ether, 10 : 1) to afford the desired compound.

2-(*E*-3-Triethoxysilylprop-2-enyl)dimethylsilanyloxy-3,3-dimethylbutyronitrile (16). Prepared as a colourless oil (61 mg, 34%) using triethoxyvinylsilane (5.0 eq.) as the alkene. R_f 0.11 (petrol–ether, 10 : 1); ν_{max}/cm^{-1} (film) 2972m, 2928w, 2882w, 1607w, 1479w, 1466w, 1445w, 1391w, 1366w, 1295w, 1258m, 1166m, 1103s, 1080s, 1035m, 956m, 887w, 957m, 772m; δ_H (400 MHz; $CDCl_3$) 0.23 (3 H, s) and 0.25 (3 H, s, $Si(CH_3)_2$), 1.02 (9 H, s, $C(CH_3)_3$), 1.23 (9 H, t, *J* 7.0, 3 × CH_2CH_3), 1.82–1.97 (2 H, m, $SiCH_2$), 3.82 (6 H, q, *J* 7.0, 3 × C*H*$_2$CH$_3$), 4.03 (1 H, s, CHCN), 5.34 (1 H, dt, *J* 18.5, 1.5, =C*H*Si), 6.43 (1 H, dt, *J* 18.5, 8.0, CH_2CH=); δ_C (100 MHz; $CDCl_3$) −2.6 (q), −2.3 (q), 18.2 (q), 24.9 (q), 28.9 (t), 35.9 (s), 58.4 (t), 71.0 (d), 119.0 (s), 119.4 (d), 148.3 (d); *m*/*z* (ESI$^+$) 432 (MNH_4^+·MeCN, 100%), 396 (MNa^+, 3); HRMS (ESI$^+$) 374.2189 (MH^+. $C_{17}H_{36}NO_4Si_2$ requires 374.2183).

2-(*E*-Cinnamyl)dimethylsilanyloxy-3,3-dimethylbutyronitrile (17). Prepared as a colourless oil (70 mg, 51%) using styrene (1.0 eq.) as the alkene. R_f 0.21 (petrol–ether, 10 : 1); ν_{max}/cm^{-1} (film) 2964m, 2238w, 1368w, 1255m, 1105s, 1035w, 993m, 860s, 754m, 694m; δ_H (400 MHz; $CDCl_3$) 0.28 (3 H, s) and 0.30 (3 H, s, $Si(CH_3)_2$), 1.05 (9 H, s, $C(CH_3)_3$), 1.87 (1 H, dd, *J* 18.5, 8.0) and 1.91 (1 H, dd, *J* 18.5, 8.0, $SiCH_2$), 4.07 (1 H, s, CHCN), 6.25 (1 H, dt, *J* 15.5, 8.0, CH_2CH=), 6.36 (1 H, d, *J* 15.5, =C*H*Ph), 7.27–7.42 (5 H, m, Ph); δ_C (100 MHz; $CDCl_3$) −2.4 (q), −2.2 (q), 23.3 (t), 25.0 (q), 36.0 (s), 71.0 (d), 119.1 (s), 125.1 (d), 125.6 (d), 126.5 (d), 128.7 (d), 130.1 (d), 137.4 (s); *m*/*z* (FI$^+$) 287 (M^+, 100%); HRMS (FI$^+$) 287.1709 (M^+. $C_{17}H_{25}NOSi$ requires 287.1700).

2-(*E*-4-Nitrocinnamyl)dimethylsilanyloxy-3,3-dimethylbutyronitrile (18). Prepared as a colourless oil (63 mg, 40%) using 4-nitrostyrene (1.0 eq.) as the alkene. R_f 0.24 (petrol–ether, 5 : 1); ν_{max}/cm^{-1} (film) 2965s, 2874m, 2446w, 1639s, 1595s, 1515s, 1478m, 1398m, 1368m, 1341s, 1257s, 1182m, 1108s, 1034m, 986m, 936w, 844s, 799s, 749m, 715m; δ_H (400 MHz; $CDCl_3$) 0.27 (3 H, s) and 0.29 (3 H, s, $Si(CH_3)_2$), 1.02 (9 H, s, $C(CH_3)_3$), 1.87–2.01 (2 H, m, $SiCH_2$), 4.04 (1 H, s, CHCN), 6.38 (1 H, d, *J* 16.0, =C*H*Ar), 6.49 (1 H, dt, *J* 16.0, 8.0, CH_2CH=), 7.41 (2 H, d, *J* 8.5) and 8.13 (2 H, d, *J* 8.5, Ar); δ_C (100 MHz; $CDCl_3$) −2.2 (2 × q), 24.3 (t), 24.8 (q), 35.9 (s), 65.8 (d), 119.0 (s), 124.0 (d), 125.9 (d), 128.1 (d), 131.3 (d), 144.5 (s), 146.1 (s); *m*/*z* (FI^+) 332 (M^+, 100%); HRMS (FI^+) 332.1556 (M^+. $C_{17}H_{24}N_2O_3Si$ requires 332.1551).

2-(*E*-3-Methoxycarbonylprop-2-enyl)dimethylsilanyloxy-3,3-dimethylbutyronitrile (19). Prepared as an orange oil (56 mg, 44%) using methyl crotonate (1.0 eq.) as the alkene. R_f 0.17 (petrol–ether, 5 : 1); ν_{max}/cm^{-1} (film) 2964m, 2239w, 1720s, 1642m, 1479m, 1436m, 1399m, 1368m, 1323m, 1262m, 1204m, 1103m, 1047m, 953w, 920m, 837m, 758m, 734m, 690m; δ_H (400 MHz; $CDCl_3$) 0.26 (3 H, s) and 0.29 (3 H, s, $Si(CH_3)_2$), 1.02 (9 H, s, $C(CH_3)_3$), 1.84–1.97 (2 H, m, $SiCH_2$), 3.72 (3 H, s, OCH_3), 4.01 (1 H, s, CHCN), 5.77 (1 H, dt, *J* 15.5, 1.5, =CHCO), 7.02 (1 H, dt, *J* 15.5, 8.5, CH_2CH=); δ_C (100 MHz; $CDCl_3$) −2.4 (q), −2.1 (q), 24.1 (t), 24.9 (q), 35.9 (s), 51.3 (q), 71.0 (d), 118.8 (s), 120.4 (d), 145.3 (d), 166.9 (s); *m*/*z* (ESI^+) 328 (MNH_4^+·MeCN, 100%), 307 (22), 292 (MNa^+, 4); HRMS (ESI^+) 270.1527 (MH^+. $C_{13}H_{24}NO_3Si$ requires 270.1525).

(3*R,4*R**,5*R**)-6,6-Dimethyl-3-phenylhept-1-ene-4,5-diol (27).** A solution of aldehyde **22** (120 mg, 0.41 mmol) in benzene (8 mL) was heated at 80 °C for 3.5 d. The mixture was cooled and the solvent removed *in vacuo* to yield the *dioxasilolane* (**25**). [δ_H (200 MHz; C_6D_6) 0.07 (3 H, s) and 0.22 (3 H, s, $Si(CH_3)_2$), 1.07 (9 H, s, $C(CH_3)_3$), 3.48 (1 H, dd, *J* 8.5, 5.0, C*H*Ph), 3.95 (1 H, d, *J* 5.0, *t*-BuC*H*), 4.51 (1 H, t, *J* 5.0, C*H*(O)CHPh), 5.16 (1 H, dd, *J* 10.0, 2.0) and 5.24 (1 H, ddd, *J* 17.0, 2.0, =CH_2), 6.19–6.50 (1 H, m, C*H*=CH_2), 7.15–7.55 (5 H, m, Ph)]. The crude dioxasilolane was dissolved in THF (16 mL), the mixture was cooled to 0 °C and TBAF (1.03 mL, 1.0 M solution in THF, 1.03 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 °C, warmed to RT and then stirred for a further 1.5 h. The reaction was quenched by the addition of ammonium chloride solution (saturated, aqueous, 30 mL) and then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with brine (80 mL) and dried over magnesium sulfate. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol–ethyl acetate, 10 : 1) to afford the *title compound* (**27**, 54 mg, 56%) as a colourless oil. R_f 0.32 (petrol–ethyl acetate, 4 : 1); ν_{max}/cm^{-1} (film) 3399br, 2963s, 2891m, 2232w, 1659w, 1370s, 1257s, 1104m, 843m, 804m; δ_H (500 MHz; $CDCl_3$) 0.99 (9 H, s, $C(CH_3)_3$), 1.82 (1 H, br s) and 2.31 (1 H, br s, 2 × OH), 3.44 (1 H, d, *J* 2.5, *t*-BuC*H*), 3.58 (1 H, t, *J* 9.0, CHPh), 4.06 (1 H, dd, *J* 9.0, 2.5, C*H*(OH)CHPh), 5.20 (1 H, d, *J* 10.0) and 5.26 (1 H, d, *J* 17.0, =CH_2), 6.05 (1 H, ddd, *J* 17.0, 10.0, 9.0, C*H*=CH_2), 7.29–7.37 (3 H, m) and 7.38–7.46 (2 H, m, Ph); δ_C (125 MHz; $CDCl_3$) 26.3 (q), 35.1 (s), 55.8 (d), 71.4 (d), 76.2 (d), 117.7 (t), 127.3 (d), 128.5 (d), 129.1 (d), 138.3 (d), 140.7 (s); *m*/*z* (CI^+) 252 (MNH_4^+, 100%), 236 (31), 119 (42), 131 (84), 118 (72); HRMS (CI^+) 252.1962 (MNH_4^+. $C_{15}H_{26}NO_2$ requires 252.1964).

(2*R*)- and (2*S*)-[(2*R*,6*S*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]-2-hydroxyacetonitrile (29) and (30)

To a stirred solution of aldehyde **28**[20] (12.7 g, 62.1 mmol) in THF (25 mL) at 5 °C was added a solution of potassium cyanide (4.86 g, 74.7 mmol) in water (25 mL). A solution of sodium hydrogen sulfite (saturated, aqueous, 40 mL) was added dropwise over 10 min and then stirring was continued for 2 h. The reaction mixture was warmed to RT and extracted with ether (3 × 50 mL). The combined organic layers were washed successively with hydrochloric acid (5.0 M, 100 mL) and brine (100 mL) and then dried over magnesium sulfate and concentrated *in vacuo* to afford the *title compounds* (**29** and **30**, 3 : 2 ratio, 12.5 g, 87%) as a colourless, viscous oil that solidified on standing to a white, waxy solid, mp 74 °C. ν_{max} (KBr)/cm^{-1} 3417br, 2951m, 2235w, 1378m, 1146s, 1035m, 946m, 874m; δ_H (400 MHz; $CDCl_3$) 1.30 (3 H, s, CH_3, **29**), 1.31 (3 H, s, CH_3, **30**), 1.34 (3 H, s, CH_3, **30**), 1.36 (3 H, s, CH_3, **29**), 3.27 (3 H, s, OCH_3, **29**), 3.28 (3 H, s, OCH_3, **30**), 3.33 (3 H, s, OCH_3, **30**), 3.35 (3 H, s, OCH_3, **29**), 3.52 (1 H, dd, *J* 11.0, 3.5, C*H*H′, **29**), 3.67 (1 H, dd, *J* 11.0, 3.5, C*H*H′, **30**), 3.74 (1 H, t, *J* 11.0, CH*H*′, **30**), 3.85 (1 H, t, *J* 11.0, CH*H*′, **29**), 4.11–4.17 (2 H, m, 2 × CHO, **29**/**30**), 4.38 (1 H, d, *J* 2.5, C*H*(OH), **29**), 4.45 (1 H, d, *J* 6.5, C*H*(OH), **30**); δ_C (100 MHz; $CDCl_3$) 17.4 (4 × q), 48.2 (2 × q), 48.3 (2 × q), 58.6 (t), 59.8 (t), 61.4 (d), 61.9 (d), 67.5 (d), 68.0 (d), 98.1 and 98.3 (2 × s), 99.8 and 100.0 (2 × s), 117.6 (2 × s); *m*/*z* (FI^+) 231 (M^+, 70%), 201 (15), 157 (30), 115 (100), 70 (25); HRMS (FI^+) 231.1111 (M^+. $C_{10}H_{17}NO_5$ requires 231.1101).

Allylchlorodiphenylsilane

Copper(II) chloride was recrystallised from hydrochloric acid (2.5 M) and then dried under high vacuum for 18 h at 150 °C. A two-necked flask was then charged with a portion of this copper(II) chloride (0.54 g, 4.0 mmol) and anhydrous copper(I) iodide (20 mg, 0.11 mmol). The flask was equipped with a Schlenk filter attached to a second flask and all joints were sealed with PTFE tape. The apparatus was evacuated under high vacuum for 3 h and purged with argon several times; anhydrous THF (7.5 mL) was then added followed by allyldiphenylsilane[1] (435 mg, 2.0 mmol). The red/orange suspension was stirred for 20 h at RT, the mixture becoming light brown in colour after 2 h. At the end of the reaction the apparatus was inverted through the Schlenk filter and the inorganic residues filtered off by suction under argon to afford a solution of allylchlorodiphenylsilane in THF.

Typical DIBAL–ene–TBAF sequence, used to prepare 35/36 and 47/48

To a stirred solution of silyloxycyanohydrin (**31**/**32** or **43**/**44**, 1.02 mmol) in dichloromethane (20 mL) at −78 °C was added DIBAL (1.52 mL, 1.0 M solution in dichloromethane, 1.52 mmol) and the solution was stirred for 1 h. A solution of tartaric acid in methanol (saturated, 6 mL) was then added and the mixture stirred for a further 30 min then warmed to RT. The mixture was partitioned between water (50 mL) and ether (100 mL) and the aqueous component was extracted with ether (3 × 60 mL). The combined organic extracts were then washed successively

with tartaric acid solution (saturated, aqueous, 60 mL) and brine (60 mL) and dried over magnesium sulfate. The residue was concentrated *in vacuo* to afford the crude silyloxyaldehydes (**33**/**34** or **45**/**46**) which were then dissolved in C_6D_6 and heated at 80 °C in a sealed tube. Heating was continued until ^{1}H NMR analysis indicated disappearance of the aldehyde resonance (16 h to 5 d) whereupon the solution was cooled and the solvent evaporated *in vacuo*. The crude siladioxolanes were then dissolved in THF (40 mL) and the solution cooled to 0 °C. TBAF (2.19 mL, 1.0 M solution in THF, 2.19 mmol) was added dropwise and the reaction mixture was stirred at 0 °C for 30 min and at RT for a further 1.5 h. The reaction was quenched by the addition of ammonium chloride solution (saturated, aqueous, 40 mL) and the product extracted into ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (petrol–ethyl acetate, 2 : 1) to afforded the diols **35**/**36** or **47**/**48**. In the case of diols **35**/**36** some of the diol **36** was obtained in a pure form, free of diol **35**, and the subsequent reactions were performed on both the diol mixture and the separated diol **36**. In the **47**/**48** series all subsequent reactions were performed on the mixture.

(1*R*,2*S*)- and (1*S*,2*R*)-1-[(2*R*,5*R*,6*R*)-5,6-Dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]pent-4-ene-1,2-diol (35) and (36). Colourless oil (**35** and **36**, 3 : 2 ratio, 320 mg, 24% on a 4.91 mmol scale). R_f 0.37 (**35**) and 0.43 (**36**) (ethyl acetate); ν_{max} (film)/cm^{-1} 3453s br, 3076w, 2949s, 2834w, 1642w, 1449m, 1376s, 1263w, 1211m, 1123s, 1037s, 949m, 879w; δ_H (400 MHz; $CDCl_3$) 1.28 (12 H, s, 4 × CH_3, **35**/**36**), 2.31–2.37 (4 H, m, 2 × C*H*$_2$CH=, **35**/**36**), 3.27 (6 H, s, 2 × OCH_3, **35**/**36**), 3.28 (6 H, s, 2 × OCH_3, **35**/**36**), 3.42–3.48 (2 H, m, 2 × C*H*(O)CH_2O, **35**/**36**), 3.67 (2 H, dd, *J* 11.4, 3.9, 2 × C*H*H′, **35**/**36**), 3.73 (2 H, t, *J* 11.4, 2 × CH*H*′, **35**/**36**), 3.87–3.94 (2 H, m, 2 × C*H*(OH)CH_2, **35**/**36**), 3.97–4.10 (2 H, m, 2 × C*H*(OH)C(O), **35**/**36**), 5.06–5.19 (4 H, m, 2 × =CH_2, **35**/**36**), 5.80–5.91 (2 H, m, 2 × C*H*=CH_2, **35**/**36**); δ_C (100 MHz; $CDCl_3$) 17.5 (q), 17.6 (q), 17.8 (q), 17.8 (q), 37.9 (t), 38.4 (t), 48.1 (q), 48.1 (2 × q), 48.2 (q), 60.1 (t), 61.0 (t), 67.9 (d), 68.5 (d), 69.8 (d), 70.9, (d), 72.7 (d), 73.7 (d), 98.0 (s), 99.2 (s), 99.2 (s), 99.4 (s), 117.9 (t), 118.5 (t), 134.3 (d), 134.5 (d); *m*/*z* (ESI$^+$) 299 (MNa^+, 100%), 242 (15); HRMS (ESI$^+$) 299.1470 (MNa^+. $C_{13}H_{24}NaO_6$ requires 299.1465).

(1*R*,2*S*,3*S*)- and (1*S*,2*R*,3*R*)-1-[(2*R*,5*R*,6*R*)-5,6-Dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]-3-phenylpent-4-ene-1,2-diol (47) and (48). Colourless oil (**47** and **48**, 3 : 2 ratio, 71 mg, 25% on a 0.802 mmol scale). R_f 0.52 (ethyl acetate); ν_{max} (film)/cm^{-1} 3456s br, 3063w, 2948s, 2833m, 1737m, 1637w, 1601w, 1453m, 1375s, 1131s, 949m, 879s, 765w, 702m, 670m; δ_H (400 MHz; $CDCl_3$) 1.30 (12 H, s, 4 × CH_3, **47**/**48**), 3.26 (3 H, s, OCH_3, **47**), 3.28 (3 H, s, OCH_3, **48**), 3.29 (3 H, s, OCH_3, **47**), 3.30 (3 H, s, OCH_3, **48**), 3.48 (1 H, dd, *J* 11.2, 3.2, C*H*H′, **48**), 3.60 (1 H, app. t, *J* 9.2, C*H*H′, **47**), 3.65–3.75 (4 H, m), 3.84–3.81 (2 H, m) and 4.02–4.16 (4 H, m, 2 × C*H*(Ph)C*H*(OH)C*H*(OH)C*H*(O)CH*H*′, **47**/**48**), 5.12–5.23 (4 H, m, 2 × =CH_2, **47**/**48**), 5.95–6.06 (2 H, m, 2 × C*H*=CH_2, **47**/**48**), 7.22–7.40 (10 H, m, 2 × Ph, **47**/**48**); δ_C (100 MHz; $CDCl_3$) 17.6–17.8 (4 × q), 48.1–48.3 (4 × q), 53.4 (t), 53.6 (t), 60.0 (t), 61.6 (t), 67.5 (d), 69.2 (d), 70.5 (d), 71.5 (d), 74.8 (d), 98.0 (2 × s), 99.2 (2 × s), 117.5 (d), 117.6 (d), 126.9–129.1 (overlapping), 137.8 (2 × d); *m*/*z* (ESI$^+$) 375 (MNa^+, 75%), 337 (100), 277 (20), 258 (10); HRMS (ESI$^+$) 375.1770 (MNa^+. $C_{19}H_{28}NaO_6$ requires 375.1778).

Deprotection of compounds 39 and 40

To a stirred solution of aldehydes **39** and **40** (114 mg, 0.249 mmol) in 1,2-dichloroethane (2.6 mL) at RT was added a solution of trifluoroacetic acid and water (9 : 1, 0.4 mL). After 2 min the solvent was removed *in vacuo* and the residue purified by column chromatography (petrol–ethyl acetate, 1 : 1) to afford the 1,6-anhydrosugars **41** [7 mg, 9% (14% based on theoretical quantity of **39**)] and **42** [10 mg, 12% (31% based on theoretical quantity of **40**)] as waxy off-white solids.

1,6-Anhydro-3,4-di-*O*-benzyl-2-deoxy-β-D-gulose (41). R_f 0.67 (ethyl acetate); $[\alpha]_D^{21}$ −35 (*c* 0.75, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 1.62 (1 H, ddd, *J* 13.1, 10.1, 1.2, 2-H_{ax}), 2.33 (1 H, ddd, *J* 13.1, 6.8, 2.0, 2-H_{eq}), 3.64 (1 H, dd, *J* 7.5, 4.5, 6-H), 3.72 (1 H, dd, *J* 8.0, 4.5, 4-H), 3.86 (1 H, ddd, *J* 10.1, 8.0, 6.8, 3-H), 4.10 (1 H, d, *J* 7.5, 6-H′), 4.47 (1 H, t, *J* 4.5, 5-H), 4.66 (2 H, s, C*H*$_2$Ph), 4.68 (1 H, d, *J* 11.8) and 4.80 (1 H, d, *J* 11.8, C*H*$_2$Ph), 5.50 (1 H, app. s, 1-H), 7.28–7.40 (10 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$); 38.2 (t), 65.4 (t), 72.1 (t), 73.0 (t), 73.5 (d), 75.9 (d), 79.4 (d), 100.8 (d), 127.7–128.6 (overlapping), 138.4 (s), 138.6 (s); *m*/*z* (ESI$^+$) 349 (MNa^+, 100%), 317 (80); HRMS (ESI$^+$) 349.1402 (MNa^+. $C_{27}H_{36}NaO_6$ requires 349.1410).

1,6-Anhydro-3,4-di-*O*-benzyl-2-deoxy-β-D-glucose (42)[24]. R_f 0.65 (ethyl acetate); $[\alpha]_D^{21}$ −60 (*c* 0.15, $CHCl_3$), lit.[24a] $[\alpha]_D^{20}$ −55.2 (*c* 0.5, $CHCl_3$), lit.[24b] $[\alpha]_D^{25}$ −39.3 (*c* 1, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 1.94 (1 H, d, *J* 14.5, 2-H_{eq}), 2.06 (1 H, ddd, *J* 14.5, 5.8, 2.0, 2-H_{ax}), 3.43 (1 H, s, 4-H), 3.65 (1 H, d, *J* 5.8, 3-H), 3.73 (1 H, t, *J* 6.8, 6-H), 4.20 (1 H, dd, *J* 6.8, 1.2, 6-H′), 4.44 (1 H, d, *J* 12.1) and 4.54 (1 H, d, *J* 12.1, C*H*$_2$Ph), 4.57 (1 H, d, *J* 12.2, C*H*HPh), 4.58 (1 H, d, *J* 6.8, 5-H), 4.62 (1 H, d, *J* 12.2, CH*H*′Ph), 5.59 (1 H, s, 1-H), 7.28–7.40 (10 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 33.0 (t), 64.7 (t), 71.1 (t), 71.2 (t), 72.3 (d), 73.9 (d), 77.2 (d), 99.9 (d), 127.5–128.5 (overlapping), 138.2 (2 × s); *m*/*z* (ESI$^+$) 349 (MNa^+, 100%).

Deprotection of compounds 51 and 52

To a mixture of aldehydes **51** and **52** (10 mg, 0.019 mmol) was added a solution of acetic acid/water (2 : 1, 1 mL) and the mixture was stirred at 100 °C for 2 h. The mixture was then cooled to RT, concentrated *in vacuo* (high vacuum line) for 18 h, and the residue purified by column chromatography (petrol–ethyl acetate, 3 : 1 → ethyl acetate) to afforded the sugar derivatives **53** [3.5 mg, 47% (78% based on theoretical quantity of **51**)] and **54** [2 mg, 27% (66% based on theoretical quantity of **52**), 52(α):48(β) anomeric mixture] as waxy off-white solids.

1,6-Anhydro-3,4-di-*O*-benzyl-2-deoxy-2-*C*-phenyl-β-D-idose (53). R_f 0.81 (ethyl acetate); $[\alpha]_D^{21}$ −19 (*c* 0.3, $CHCl_3$); ν_{max} (film)/cm^{-1} 3418m br, 2962s, 1729w, 1496w, 1454m, 1100s, 873w, 800m, 699m; δ_H (500 MHz; $CDCl_3$) 2.98 (1 H, d, *J* 9.8, 2-H), 3.78 (1 H, dd, *J* 7.5, 4.5, 6-H), 3.86 (1 H, dd, *J* 8.0, 4.5, 4-H), 3.94 (1 H, dd, *J* 9.8, 8.0, 3-H), 4.10 (1 H, d, *J* 10.8, C*H*H′Ph), 4.29 (1 H, d, *J* 7.5, 6-H′), 4.49 (1 H, d, *J* 10.8, CH*H*′Ph), 4.56 (1 H, t, *J* 4.5, 5-H), 4.70 (1 H, d, *J* 11.7) and 4.79 (1 H, d, *J* 11.7, C*H*$_2$Ph), 5.37 (1 H, d, *J* 1.2, 1-H), 6.98–7.50 (15 H, m, 3 × Ph); δ_C (125 MHz; $CDCl_3$) 55.7 (d), 65.7 (t), 73.0 (t), 73.8 (d), 75.0 (t), 80.2 (d), 81.4 (d), 103.5 (d), 127.2–129.3 (overlapping); *m*/*z* (ESI$^+$) 425 (MNa^+, 100%),

413(50); HRMS (ESI$^+$) 425.1722 (MNa$^+$. $C_{26}H_{26}NaO_4$ requires 425.1723).

3,4-Di-*O*-benzyl-2-deoxy-2-*C*-phenyl-D-glucose (54). R_f 0.36–0.58 (streaks) (ethyl acetate); $[\alpha]_D^{21}$ +29 (*c* 0.18, $CHCl_3$); ν_{max} (film)/cm^{-1} 3453s br, 3079w, 2949s, 2834m, 1642w, 1449m, 1376m, 1263w, 1123s, 1037s, 949w, 879m; δ_H (500 MHz; $CDCl_3$) 2.84 (1 H, dd, *J* 10.8, 8.8, 2-H, β), 3.07 (1 H, dd, *J* 11.2, 3.0, 2-H, α), 3.68 (1 H, dd, *J* 9.7, 8.5, 4-H, β), 3.69 (1 H, dd, *J* 9.8, 8.7, 4-H, α), 3.90 (1 H, dd, *J* 10.8, 8.5, 3-H, β), 3.95 (1 H, d, *J* 10.3, C*H*H′Ph), 4.06–4.26 (6 H, m, 2 × 5-H and 2 × 6-H$_2$, α/β), 4.18 (1 H, d, *J* 10.3, C*H*H′Ph), 4.36 (1 H, dd, *J* 11.2, 8.7, 3-H, α), 4.47 (1 H, d, *J* 10.3, CH*H*′Ph), 4.60 (1 H, d, *J* 10.3, CH*H*′Ph), 4.71 (1 H, d, *J* 11.0, C*H*H′Ph), 4.72 (1 H, d, *J* 11.1, C*H*H′Ph), 4.91 (1 H, d, *J* 11.0, CH*H*′Ph), 4.94 (1 H, d, *J* 11.1, CH*H*′Ph), 5.06 (1 H, d, *J* 8.8, 1-H, β), 5.30 (1 H, d, *J* 3.0, 1-H, α), 6.76–7.52 (30 H, m, 6 × Ph, α/β); δ_C (125 MHz; $CDCl_3$) 54.2 (d), 57.1 (d), 62.2 (t), 62.3 (t), 71.8 (d), 75.7 (d), 78.5 (d), 79.6 (d), 80.5 (d), 84.5 (d), 75.1–75.4 (4 × t), 94.8 (d), 97.6 (d), 127.4–130.0 (overlapping); *m*/*z* (ESI$^+$) 443 (MNa$^+$, 100%), 429 (20), 305 (20), 261 (10), 215 (10); HRMS (ESI$^+$) 443.1830 (MNa$^+$. $C_{26}H_{28}NaO_5$ requires 443.1829).

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8 Crystal data for **12**: $C_{20}H_{24}O_2Si$, $M = 324.50$, colourless plate, monoclinic, $a = 8.8918(3)$, $b = 15.1623(7)$, $c = 13.7021(5)$ Å, $V = 1832.97$ Å^3, $T = 120$ K, space group $P2_1/n$, $Z = 4$, 6513 reflections measured, 4136 independent, 2996 used for refinement ($R_{int} = 0.01$), final $wR = 0.0584$. CCDC reference number 682308. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b804752a.

9 Approximate bond lengths: Si–C, 1.89 Å (C–C, 1.54 Å); Si–O, 1.63 Å (C–O, 1.43 Å).

10 The timing and degree of association of the carbonyl oxygen with the silicon is open to speculation but the hybridisation state at the silicon atom must change from tetrahedral to trigonal bipyramidal (tbp) and back to tetrahedral as the reaction progresses; in other words, whether a tbp silicon is an intermediate or transition state is presently an open question.

11 Prepared from benzaldehyde: (i) ethyl isobutyrate, LDA, THF, −78 °C → RT over 12 h (61%); (ii) allyldiphenylsilane, $B(C_6F_5)_3$, CH_2Cl_2, reflux, 2 h (54%); (iii) DIBAL, CH_2Cl_2, −78 °C, 1 h (84%); (iv) Swern oxidation (quant.).

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14 Under similar conditions, cross-metathesis of the diphenyl analogue of **15** (see ref. 1) with triethoxyvinylsilane proceeded in 52% yield.

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